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Contract No. DA 18-108-AMC-118(A)

QUARTERLY PROGRESS REPORT NO. 3

Covering the Period

18 September - 17 December 1963

INVESTIGATION OF THE FLASHING OF AEROSOLS



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PREFACE

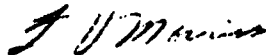
This is Quarterly Progress Report No. 3 on Contract No. DA 18-108-AMC-118(A), M.R.I. Project 2685-C, titled "Investigation of the Flashing of Aerosols." It covers the period 18 September through 17 December 1963. All information presented in the monthly letter reports is contained in the project quarterly reports.

The purpose of this project is to obtain information on aerosol flammability as a function of (a) fuel concentration, vapor pressure and particle size, (b) source of ignition, and (c) composition of the environmental gas. Additives which will tend to suppress either the ignition or the combustion of the aerosol are to be evaluated.

This one-year project is sponsored by the U. S. Army Chemical Research and Development Laboratories, Director of Weapons Systems, Physicochemical Research Division, Colloid Branch. Mr. Joseph Pistrutto is the Project Officer. Work on this program is being accomplished by Mr. Alan R. Pittaway, the principal investigator, Mr. Harry Pollock and Mr. Frank Brin: under the supervision of Dr. John W. Barger, Assistant Director, Chemistry Division.

Approved for:

MIDWEST RESEARCH INSTITUTE



F. V. Morris, Director
Chemistry Division

4 March 1964

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SUMMARY

This program is concerned with determining flammability of aerosol systems. The liquid phase material has been purified and a method of obtaining the small range of particle sizes evaluated. The explosive detonation product gas mixture has been determined to be flammable over the range of 25 to 52.5 per cent by volume. It was found that very large concentrations of QL aerosol in this gas-air mixture do not significantly change the flammability limits.

I. INTRODUCTION

This program is related to the phenomenon known as "flashing" which occurs during the explosive dissemination of combustible liquids. An analysis of the flashing phenomenon was given in Quarterly Report No. 1. The purpose of this project is to provide additional fundamental information on aerosol combustion. The information can then be applied to specific flashing problems.

A large, electrically ignited, "combustion chamber" is being used to determine the interrelationships between aerosol-fuel-particle size, concentration, vapor pressure, and environmental gas composition on aerosol flammability. A shock tube is being used to evaluate the shock strength required to ignite mixtures found to be flammable in the combustion chamber.

This report reviews the current status of the project and covers its development since the last quarterly report.

II. CURRENT PROGRESS

A. Purification of QL

It was noted in the second quarterly report that the first QL ampoule opened was under a positive pressure and had a strong penetrating odor. Because of our experience with this sample, we decided to vacuum distill the next ampoule and assay its purity.

Two documents, CRDL Technical Memorandum No. 14-15 titled, "Gas Chromatography of EZ, VX, QL, and GB," and Food Machinery and Chemical Corporation Final Report on Contract DA-11-032-ENG-7295, dated August 1961, were consulted to determine previous experience in this area.

To accomplish the distillation, we used a vacuum jacketed glass column 1 in. I.D. x 4 ft. long, packed with glass helices. A Corad constant ratio distilling head gave us a reflux ratio of about one to one. The system was operated at 1 mm. mercury pressure with a continuous nitrogen sweep through the column, head, and receiver. To assay the sample, we used a Micro-Tek, Model GC-2500R programmed temperature gas chromatograph.

Knowing that QL is compatible with Apiezon grease, the distillation system was assembled from standard fittings and stopcocks, using Apiezon N

grease for vacuum sealing. This was an error, because QL vapor and liquid are such excellent solvents for Apiezon grease. Any future distillation should be conducted in apparatus with Teflon fittings.

We were surprised when we opened the second ampoule in preparation for filling the distillation flask. There appeared to be no pressure in the ampoule, and it was comparatively free of strong odor. We took a sample of this for chromatographic analysis, and proceeded with the distillation. The distilled material was separated into three fractions, 75 ml. in the first fraction which was discarded, 275 ml. in the second which was retained, and 50 ml. left in the pot.

Problems were encountered in making quantitative assays of QL. Gas chromatograph columns prepared by the method in the cited references do not produce a column with a known amount of stationary phase. Consequently, the column time constants and curve area relationship for previously reported columns cannot be used. Lacking a known sample of any material or constituent to calibrate our column, a request for a "known" was made to CRDL. The distillation procedure should produce some reasonably purified material and we elected to use this as a qualitative reference standard. We have since received a pure sample of TR which will be a significant aid in calibrating our columns and correlating with the published data.

The chromatograph of the original material and of each of the three fractions indicated that the distillation increased the height of the QL peak but that all of the samples were very similar. The distillation primarily reduced the percentage of high boiling impurities.

In view of the marked difference between these first two ampoules (i.e., internal pressure and odor), and lack of a major improvement in purity of the second ampoule on distillation, we have decided not to distill future ampoules unless they exhibit strong odor or pressure. None of the ampoules opened subsequently have shown signs of deterioration.

B. Particle Size Studies

Particle size studies were interrupted due to (1) corrosion of the pump by the glycerine-water mixture, and (2) decomposition of QL in the first ampoule. This study was reinitiated during this period using the vacuum distilled QL.

Previous studies had indicated that the 1582 nozzle operated best between 4,000 to 5,000 psi for production of small particle sizes. Therefore, initial studies on QL were initiated at 4,000 psig.

The initial effort encountered difficulty when it was observed that the injector pump would not hold a pressure. Disassembly revealed that the check valve was inoperable due to a deformed Teflon O-ring. The check valve assembly was worked over in the machine shop to reduce the amount of stretching required to place the Teflon O-ring in position.

Unfortunately, this O-ring is the check valve. The O-ring rests in a "vee" like the contact between a belt and a pulley. The base of the vee is a small slot which allows liquid to be pumped in under the O-ring. Pressure beneath the O-ring forces liquid into the discharge side. When the pump piston retreats, the pressure downstream of the O-ring forces it into the vee creating a seal, which prevents backflow into the pump piston chamber.

The reworked valve allows us to place an O-ring on the vee without stretching it to the point that it will not seal. It still leaks back, but it holds well enough that the system can be pumped up to pressure.

The initial trial runs at 4,000 psig injector pressure disclosed that we were not getting any particles to the top of the chamber, in contrast to our experience with the glycerine-water mixture. It also disclosed that we apparently had a wider spread in the particle sizes than we had been experiencing with the glycerine-water. This meant that we had two new problems: (1) a change in the size distribution, and (2) a change in the distribution of particles within the chamber. The arithmetic mean particle size appeared to be about the same as with the glycerine-water mixture.

Originally, it was the intent of the project to characterize the aerosol produced by a known technique, which was to be within acceptable size limits. At this point, our problem reversed itself and became one of finding a technique to produce an acceptable aerosol. The problem was attacked in three ways: first, we secured the advice of senior MRI staff members through a formal briefing followed by an intensive discussion period; second, we contacted injector manufacturers and others for recommendations; and third, we instituted a much more rigorous technique for appraising the aerosols being produced.

The MRI senior staff presentation resulted in the recommendation that the nozzles and pump be evaluated with diesel fuel to determine if the problem was associated with some unusual feature of QL's liquid properties. It was also recommended that the nozzle spray angle be changed and that the combustion chamber spray distribution pattern be examined. However, the over-all view was that the approach being taken was sound and that the project should continue on its present course of action.

The American Bosch Arma Corporation was contacted to obtain recommendations on a nozzle which would produce smaller particles. After several discussions it was recommended that we try either an ADN 8SD24/4462 modified to an annular area of 0.23 mm. or an ADN 15SD35/4463 modified to an annular area of 0.13 mm. Both of these were ordered. These nozzles fit the original nozzle holder and are operated with the injector pump.

American Bosch Arma further stated that the reproducibility of our sprays would be improved if we used a mechanical pump system rather than our manual injection technique. They also stated that some improvement in particle size could be gained by going to pressures higher than 5,000 psig, our present limit.

The 8SD24 nozzle was evaluated first because the included angle of the spray with this nozzle is only 8 degrees. It was believed that this would improve the throw of the spray and assist in obtaining a uniform aerosol in the chamber.

A particle size analysis and a spray distribution study was made on this nozzle with 5,000 psig pressure on the injected liquid. Using QL it was found that 50 per cent of all spray particles were below 10 μ in diameter and 80 per cent were below 20 μ . The spray pattern in the chamber was good. The aerosol generated remains airborne; the walls of the chamber remain dry.

Pending receipt of the 8SD24 nozzle, an evaluation was made of the particle size produced in QL and diesel fuel sprays under similar conditions. It was found that the diesel fuel spray particle size was indeed smaller but that the particle size and particle size distribution in both sprays was similar.

It was decided that the spray produced by the 8SD24 nozzle was close enough to the desired particle size to initiate the aerosol flammability study in the combustion chamber.

C. Combustion Chamber Studies

1. Detonation product gas flammability: Pending preparation of the distilled QL for particle size studies, the combustion chamber was used to determine flammability limits for the detonation product gas mixture. To check the validity of the data to be determined, we ran initial experiments with methane-air mixtures for comparison of our upper and lower limit data with literature values.

Coward and Jones in Bureau of Mines Bulletin No. 503 report that the methane-air upper and lower limits in similar equipment are 5.75 and 13.6 per cent methane, respectively. Our data in the combustion chamber show that the lower limit is between 5 and 6 per cent and the upper limit between 13 and 13.5 per cent. Mixing was by allowing the air to "jet" into the partially evacuated chamber containing only methane, and then waiting 30 min. for additional diffusive mixing. The data show reasonable agreement for this type of measurement, especially considering the lack of assurance of absolute mixing.

Measurements were then made on the synthetic detonation product gas. The detonation product gas was formed from both tank gas and vaporized liquids, as described in Quarterly Report No. 2. The upper flammability limit of this mixture was found to be between 52.5 and 55 per cent of the gas by volume with air. The lower limit is between 22.5 and 25 per cent gas by volume with air. The interval between the two percentages does not necessarily represent the limit of our ability to measure the accuracy of the limit mixtures. They are only the last points in successive determinations of halving the difference between mixtures which "fired" and mixtures which "did not fire."

2. Aerosol flammability: Having obtained values for the detonation product gas flammability limits and the spray characteristics of an injector nozzle, we were now able to undertake aerosol flammability studies.

The aerosolization of about 1.56 ml. of QL formed a stoichiometric mixture with the volume of air contained in the combustion chamber. This is equivalent to 0.106 gm/liter. It would be expected that the lower limit would be on the order of 0.05 gm/liter and the upper limit about 0.180 gm/liter at the small aerosol particle size. If the QL were vaporized, these values would correspond to about 0.475 per cent and 1.72 per cent by volume, respectively.

To determine the flammability limits of the three component mixtures, it is necessary that one component be held constant and the other two varied. We elected to hold the quantity of QL constant in a given determination and vary the detonation product gas-air mixture to determine limits. The procedure was as follows: Taking one pump stroke of QL (0.95 ml.) as an initial constant quantity of aerosol, we injected this into a gas mixture and activated the spark ignitor. The result was rated either "fire" or "no fire" depending on whether or not flame front propagated to the bottom of the chamber. Knowing the flammability limits of the detonation product-air mixtures alone, we could then judge in which direction to change the relative concentration of these two gases to obtain a result opposite to the first one, i.e., if we had a "fire" we next attempted to get a "no fire" mixture. The establishment of a "bracket" defined

that the limit being sought was somewhere between these two values. By subsequently halving the difference between any two dissimilar results (fire, no fire), we could narrow down the position of the limit. After determining the limit for one QL concentration, we then changed to another and repeated the determination of limits by changing the gas mixture. Thus, all possible values and interrelationships of the three variables in the system are systematically examined.

The upper and lower flammability limits of the system can be examined in an identical manner. One only has to realize that as you move continuously in one direction along a constant concentration line of one component, the system will change from nonflammable to flammable and back to nonflammable.

The raw data thus consist of a series of gas mixtures containing a liquid-phase concentration of an aerosol. To present these data, we have elected to convert all values to mole per cent. This corrects the gas volumes for day-to-day variations in pressure and temperature and at the same time places all three components on a comparable footing.

Data obtained to date are presented in Fig. 1. Note the unusual shape of the rich limit curve. It would be expected that if the two fuels competed equally for the oxygen in the air, the flammability curve would approach a straight line between the two respective limit values of the two fuels. The curve states that the presence of the aerosol has not changed the flammability limit of the system! This means that the QL aerosol is not significantly involved with the transfer of the flame front through the system! This conclusion would support the theory that the combustion of the aerosol occurs during the combustion of the detonation product gases and that aerosol ignition is caused by the product gas combustion.

Observation of the combustion reveals that the flame propagation velocity of the mixture is greatly reduced in the presence of the aerosol. The color changed from the normal blue to orange. The flame front changed from planar to cellular.

During the study with aerosols, we experienced an unexpected change in the lower limit flammability of the detonation product gas-air mixture. No explanation can be offered at this time, but we suspect that the chamber has become contaminated with the combustion products of QL. Some of these could have a significant influence on the gas flammability.

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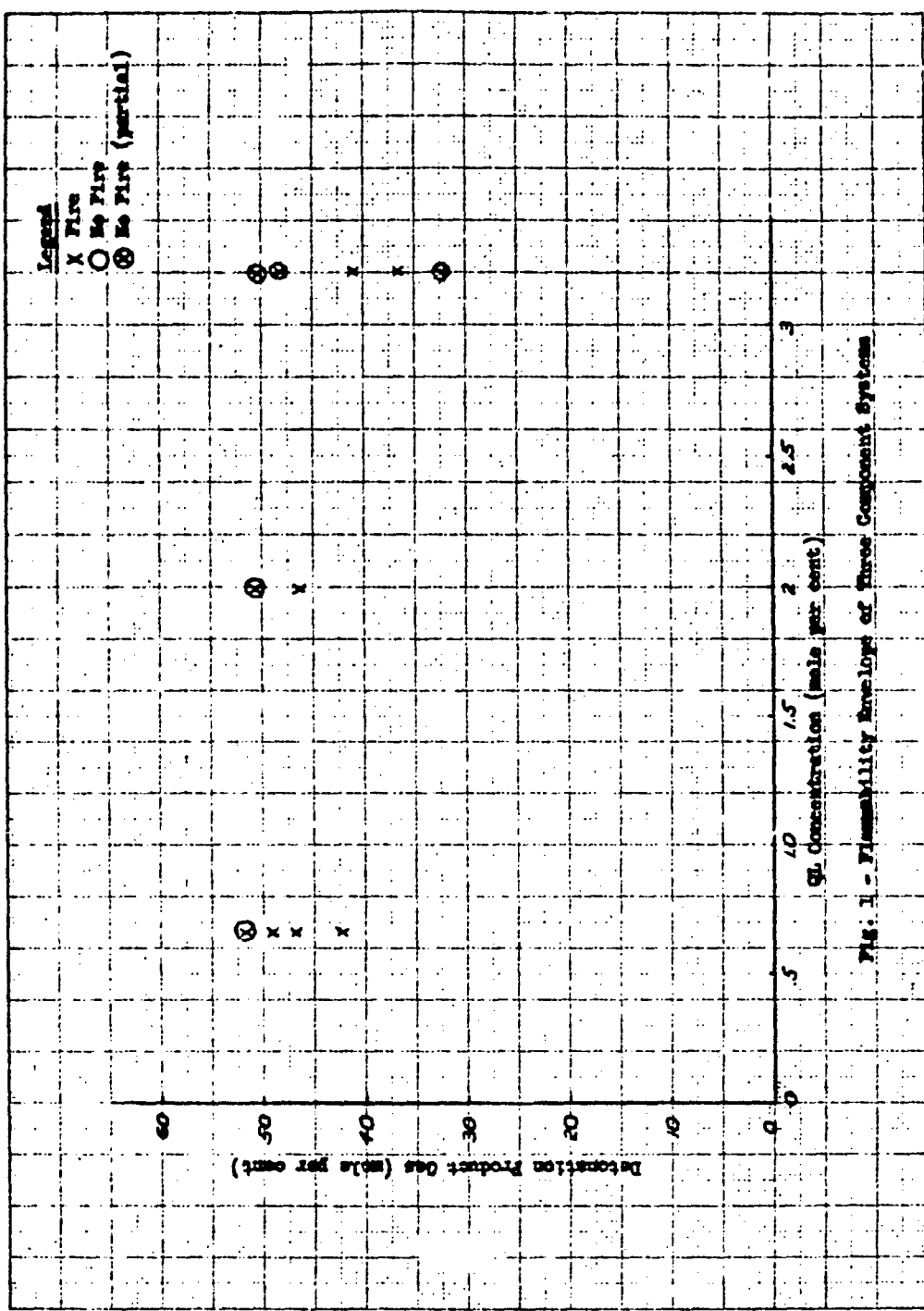


Fig. 1 - Flammability Envelope of Three Component System

D. Shock Tube Studies

Installation of the shock tube was undertaken during this period. The tube was assembled for leak testing complete with the major portion of the plumbing and other accessories. Several leaks were found. All joints between sections leaked and many of the welds leaked. Close examination revealed that many of the flanges had been warped in welding. This is relatively minor and a simple refacing will cure this. Leaking welds are a more serious criticism but vacuum-tight welding of stainless steel is quite difficult. The most difficult leak was the Marman clamp joints between two of the sections.

The leaks at the Marman clamp joints were of two types, that due to warpage of the flange and that due to the inability of the clamp to "draw up" against a reasonable bending moment of the tube. It was decided to eliminate them entirely rather than try to rework the joint, substituting the less complex straight flange used on the other sections.

In the meantime, initial tests were made to establish thickness requirements on the rupture diaphragms. These tests have shown that 0.009 in. brass sheet will hold the maximum anticipated pressure.

III. FUTURE WORK

The immediate work plans are to obtain data on the aerosol lean flammability limits, to determine the QL-air limit, examine the effects of inhibition, and to obtain data on the effects of shock wave induced ignition.

AD Accession No. Missouri Research Institute, Kansas City, Missouri INVESTIGATION OF THE FLASHING OF AEROSOLS - Alan R. Pittman Quarterly Report No. 3, 4 March 1964, 9 pp - 1 illus. Contract DA 19-108-AMC-118(A)	1. Aerosol ^o 2. Chemical warfare agents 3. Aerosol genera- tions ^o 4. Explosive gases 5. Explosions 6. Combustions ^o 7. Ignition ^o 8. Shock waves 9. Inhibition 10. Contract DA 19- 108-AMC-118(A)	AD Accession No. Missouri Research Institute, Kansas City, Missouri INVESTIGATION OF THE FLASHING OF AEROSOLS - Alan R. Pittman Quarterly Report No. 3, 4 March 1964, 9 pp - 1 illus. Contract DA 19-108-AMC-118(A)	1. Aerosol ^o 2. Chemical warfare agents 3. Aerosol genera- tions ^o 4. Explosive gases 5. Explosions 6. Combustions ^o 7. Ignition ^o 8. Shock waves 9. Inhibition 10. Contract DA 19- 108-AMC-118(A)	AD Accession No. Missouri Research Institute, Kansas City, Missouri INVESTIGATION OF THE FLASHING OF AEROSOLS - Alan R. Pittman Quarterly Report No. 3, 4 March 1964, 9 pp - 1 illus. Contract DA 19-108-AMC-118(A)	1. Aerosol ^o 2. Chemical warfare agents 3. Aerosol genera- tions ^o 4. Explosive gases 5. Explosions 6. Combustions ^o 7. Ignition ^o 8. Shock waves 9. Inhibition 10. Contract DA 19- 108-AMC-118(A)
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